Synthesis, Spectroscopy, and *X*-Ray Crystallographic Analysis of (η^3-Dithiobenzoato-*SCS'*)oxo(trithioperoxybenzoato-*S,S'S''*)molybdenum(IV) and μ-Oxo-bis[bis(dithiobenzoato-*SS'*)oxomolybdenum(V)]

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The title oxomolybdenum complexes [$Mo^{IV}O(S_2CPh)(S_3CPh)$] and [$Mo^{V}_2O_3(S_2CPh)_4$] have been obtained by the reaction of $Na_2[MoO_4]$ with [NEt_2H_2][S_2CPh] in an acidic aqueous medium, followed by chromatographic separation on a silica column using carbon disulphide as eluant. They have been characterized by elemental analysis, i.r. and electronic spectroscopy. A single-crystal *X*-ray structure analysis of [$Mo_2O_3(S_2CPh)_4$] reveals a structure in which two $Mo^{V}O(S_2CPh)_2$ moieties are oxo-bridged. The monoclinic crystal, space group $C2/c$, has cell dimensions a = 38.951(9), b = 10.678(4), c = 16.777(3) Å, β = 111.28(1)°, and Z = 8. Block-diagonal least-squares refinement, based on 2 340 independent reflections with $|F| > 3\sigma(F)$, yields an R factor of 0.070. An *X*-ray structure analysis of [$MoO(S_2CPh)(S_3CPh)$] has shown the presence of η^3-dithiobenzoato- and trithioperoxybenzoato-ligands co-ordinated to oxomolybdenum(IV). The crystals are monoclinic, space group $P2_1/c$, with cell dimensions a = 15.614(2), b = 8.441(1), c = 13.125(2) Å, β = 104.46(1)°, and Z = 4. Least-squares refinement, based on 3 767 independent reflections with $|F| > 3\sigma(F)$, yields an R factor of 0.035.

THE co-ordination compounds of molybdenum in its higher oxidation states (IV—VI) have attracted much interest due to their potential as model compounds for molybdoenzymes.[1] In particular, there is a growing interest in the chemistry of oxomolybdenum complexes containing sulphur as a ligating atom in connection with the active sites of some molybdenum oxidases; recent extended *X*-ray absorption fine structure spectroscopy (EXAFS) studies on xanthine [2] and sulphite [3] oxidases have indicated the presence of ligating oxo-groups and sulphur atoms in these molybdoenzymes.

The chemistry of oxomolybdenum complexes of dithiocarbamate, S_2CSR, dithiophosphate, and dithiophosphinate has been widely investigated.[1,4,5] However, no study of the dithioaromatic acid derivatives of oxomolybdenum has been reported, although a few reports have appeared on tetrakis(dithiobenzoato)molybdenum(IV).[6,7]

This paper reports the isolation and properties of μ-oxo-bis[bis(dithiobenzoato)oxomolybdenum(V)] (1), (dithiobenzoato)oxo(trithioperoxybenzoato)molybdenum(IV) (2), and bis(dithiobenzoato)oxomolybdenum(IV). The *X*-ray molecular structures of the first two complexes are also described. A preliminary report of the structure of (dithiobenzoato)oxo(trithioperoxybenzoato)molybdenum(IV) has appeared.[8]

EXPERIMENTAL

Materials.—Diethylammonium dithiobenzoate [NEt_2H_2][S_2CPh] was obtained as red microcrystals from the reaction of diethylamine with dithiobenzoic acid [9] in diethyl ether. Bis(thiobenzoyl) disulphide was prepared by the equimolar reaction of [NEt_2H_2][S_2CPh] with iodine in ethanol at −5 °C; a pink precipitate which formed in 10 min was collected, washed with ethanol, and dried *in vacuo*, m.p. 80 °C (Found: C, 54.55; H, 3.3. Calc. for $C_{14}H_{10}S_4$: C, 54.9; H, 3.3%).

μ-Oxo-bis[bis(dithiobenzoato)oxomolybdenum(V)], [$Mo^{V}_2O_3(S_2CPh)_4$] (1).—To a stirred water–methanol (4 : 1 v/v) solution (200 cm^3) of $Na_2[MoO_4]\cdot 2H_2O$ (2.38 g, 9.83 mmol), [NEt_2H_2][S_2CPh] (2.23 g, 9.83 mmol), and Na[OCOMe] (2.01 g, 24.5 mmol), was added hydrochloric acid (1.0 mol dm^{-3}, 50 cm^3), dropwise at 0 °C. The immediate green precipitate was filtered off and recrystallized from dichloromethane–light petroleum (b.p. 30—50 °C, throughout) (3 : 1 v/v) within a few hours to yield dark green microcrystals (0.47 g, 12%), m.p. 138—145 °C (Found: C, 39.0; H, 2.35. Calc. for $C_{28}H_{20}Mo_2O_3S_8$: C, 39.45; H, 2.35%).

(Dithiobenzoato)oxo(trithioperoxybenzoato)molybdenum(IV), [$Mo^{IV}O(S_2CPh)(S_3CPh)$] (2).—To an aqueous solution (200 cm^3) of $Na_2[MoO_4]\cdot 2H_2O$ (2.67 g, 11.8 mmol), [NEt_2H_2][S_2CPh] (2.86 g, 11.8 mmol), and Na[OCOMe] (2.50 g, 30.5 mmol), was added hydrochloric acid (1.0 mol dm^{-3}, 50 cm^3), dropwise with stirring at room temperature. The resulting precipitate was filtered off, washed with water and then methanol, and dried *in vacuo* (3.13 g). An apparently green solid thus obtained was dissolved in carbon disulphide and the solution was chromatographed on a silica column using the same solvent as eluant to give pink, dark blue, dark brown, and orange bands. The orange fraction was evaporated to dryness under reduced pressure. The resulting product was recrystallized from dichloromethane–light petroleum (3 : 1 v/v) to afford orange plates of (2) (0.16 g, 6%), m.p. 161—162 °C (Found: C, 37.3; H, 2.25. Calc. for $C_{14}H_{10}MoOS_5$: C, 37.35; H, 2.25%). This compound was also obtained by recrystallization of the green solid from dichloromethane–light petroleum (3 : 1 v/v). The three other fractions were treated similarly to give, respectively, a pink powder, dark blue needles, and black needles. These products were identified as $(PhCS_2)_2$, [$Mo^{IV}(S_2CPh)_4$],[6,7] and [$Mo^{IV}O(S_2CPh)_2$] respectively, on the basis of elemental analyses and i.r. spectra.

Reaction of (2) *with* PR_3 (R = Ph *or* Bu^n).—An equimolar mixture of (2) (0.089 g, 0.20 mmol) and PPh_3 (0.051 g, 0.19 mmol) in dichloromethane (30 cm^3) was stirred for 1 h at room temperature. The solution was evaporated to dryness under reduced pressure. The resulting product was recrystallized from benzene–light petroleum (1 : 1 v/v) to yield black needles of [$Mo^{IV}O(S_2CPh)_2$] (0.029 g, 35%), m.p. 169—171 °C (Found: C, 40.3; H, 2.6. Calc. for $C_{14}H_{10}MoOS_4$: C, 40.2; H, 2.4%). This compound was also obtained as follows. To an aqueous solution (100 cm^3) of $Na_2[S_2O_4]$

(8.0 g, 40 mmol), was added an aqueous solution (200 cm^3) of $Na_2[MoO_4]\cdot 2H_2O$ (1.80 g, 7.44 mmol) and $[NEt_2H_2][S_2CPh]$ (1.68 g, 7.44 mmol) and the mixture stirred for 16 h at room temperature. To the yellowish green solution obtained, was added hydrochloric acid (5.0 mol dm^{-3}, 50 cm^3) at 0 °C and the resulting solution stirred for another 1 h. The resulting precipitate was filtered off and washed with water several times. After drying *in vacuo*, it was recrystallized from benzene–light petroleum (1 : 1 v/v) to yield black needles (0.17 g, 10%).

On the other hand, the reaction of (2) (0.036 g, 0.08 mmol) with an excess of PPh_3 (0.084 g, 0.32 mmol) in dichloromethane (30 cm^3) gave a yellowish green oil which was washed with ethanol. The precipitate obtained was washed with diethyl ether and dried *in vacuo* to give a yellow powder of $[Mo^{IV}O(S_2CPh)_2(PPh_3)]$ (0.020 g, 37%), m.p. 103—107 °C (Found: C, 56.15; H, 4.1. Calc. for $C_{32}H_{25}MoOPS_5$: C, 56.45; H, 3.7%). To a benzene solution (40 cm^3) of (2) (0.128 g, 0.28 mmol) was added PBu^n_3 (0.115 g, 0.67 mmol) dissolved in the same solvent (10 cm^3). After stirring for 1 h at room temperature, the solution was evaporated to dryness under reduced pressure. The resulting residue was washed with ethanol, then with diethyl ether, and dried *in vacuo* to give a yellow powder of $[Mo^{IV}O(S_2CPh)_2(PBu^n_3)]$ (0.065 g, 32%), m.p. 162—164 °C (decomp.) (Found: C, 50.3; H, 6.15. Calc. for $C_{26}H_{37}MoOPS_4$: C, 50.3; H, 6.0%).

Spectra.—Infrared spectra were measured with a Hitachi 215 spectrophotometer, electronic absorption spectra with a Union SM-401 spectrophotometer. The ^{13}C n.m.r. spectrum of (2) was recorded in [$^2H_1$]chloroform at 15.03 MHz using the pulse Fourier-transform technique on a JEOL FX 60 spectrometer at 34 °C. The chemical shifts were measured relative to $SiMe_4$ as internal standard.

Crystal-structure Determinations of (1) *and* (2).—The space group and initial unit-cell parameters were determined from oscillation and Weissenberg photographs. Accurate unit-cell parameters were obtained from the least-squares fit of the angular co-ordinates of 20 reflections with 2θ values from 24 to 37° for (1) and from 26 to 36° for (2) which were measured on a computer-controlled Rigaku four-circle diffractometer using graphite-monochromatized Mo-K_α (λ = 0.710 69 Å) radiation.

Intensity data were collected up to 45° for (1) and 60° for (2) using the $\omega-2\theta$ scan technique at a 2θ scan rate of 2° min^{-1}. The scan width in 2θ was $(0.8 + 0.34\tan\theta)°$ for (1) and $(2.0 + 0.68\tan\theta)°$ for (2), and 30-s background counts were taken on either side of each scan. Five check reflections were monitored after every 50 reflections. No significant intensity variation was observed during the data collection. The intensities were corrected for Lorentz and polarization effects. No corrections were made for absorption. The crystal dimensions were approximately 0.11 × 0.12 × 0.04 mm for (1) and 0.15 × 0.18 × 0.18 mm for (2). A total of 4 237 independent reflections was recorded for (1), of which 2 340 had structure amplitudes larger than three times their standard deviations. Of the 4 872 independent reflections measured for (2), 3 767 had structure amplitudes larger than three times their standard deviations. These were used in the subsequent calculations.

Crystal data. (1). $M = 852.8$, Monoclinic, space group $C2/c$, $a = 38.951(9)$, $b = 10.678(4)$, $c = 16.777(3)$ Å, $\beta = 111.28(1)°$, $U = 6\,502(3)$ Å^3, $Z = 8$, $D_c = 1.742(2)$ g cm^{-3}, $F(000) = 3\,392$, μ(Mo-K_α) = 12.8 cm^{-1}.

(2). $M = 450.5$, Monoclinic, space group $P2_1/c$, $a = 15.614(2)$, $b = 8.441(1)$, $c = 13.125(2)$ Å, $\beta = 104.46(1)°$, $U = 1\,675.0(4)$ Å^3, $Z = 4$, $D_c = 1.786(1)$ g cm^{-3}, $F(000) = 896$, μ(Mo-K_α) = 13.4 cm^{-1}.

Solution and refinement of the structures. The co-ordinates of all the atoms, except hydrogen, were obtained by conventional Patterson and Fourier syntheses. Block-diagonal least-squares refinement for (1) with anisotropic thermal parameters for all the non-hydrogen atoms led to residual indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.074$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.079$. Hydrogen was inserted as a fixed atom at the calculated positions with fixed isotropic temperature factors $B = 5.0$ Å^2, assuming C–H 0.95 Å. The refinement on the basis of this model converged with $R = 0.070$ and $R' = 0.064$. For (2), the positions of all the hydrogen atoms of the phenyl rings were clarified from a difference-Fourier map based on the anisotropic refinement of all the non-hydrogen atoms. Block-diagonal least-squares refinement with anisotropic thermal parameters for all the non-hydrogen atoms and with isotropic thermal parameters for hydrogen atoms led to final residual indices $R = 0.035$ and $R' = 0.044$.

Atomic scattering factors used throughout the refinements were those of ref. 10 for non-hydrogen atoms and of Stewart *et al.*[11] for hydrogen. Anomalous dispersion corrections of the form $f = f_o + \Delta f' + i\Delta f''$ were applied to molybdenum and sulphur; $\Delta f' = -1.825$ and $\Delta f'' = 0.688$ for Mo, $\Delta f' = 0.110$ and $\Delta f'' = 0.124$ for S. Tables 1 and 2

TABLE 1

Atomic co-ordinates (× 10^4) for $[Mo^V{}_2O_3(S_2CPh)_4]$ (1), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mo(1)	735.5(4)	1 710(1)	959.1(9)
Mo(2)	1 556.5(4)	3 698(2)	2 041.6(9)
S(1)	247(1)	967(4)	−405(3)
S(2)	425(1)	3 516(4)	79(3)
S(3)	1 088(1)	−279(5)	1 231(3)
S(4)	1 117(1)	1 390(4)	−84(3)
S(5)	1 934(1)	1 971(4)	1 829(3)
S(6)	2 177(1)	4 509(5)	2 114(3)
S(7)	1 428(1)	4 282(4)	379(3)
S(8)	1 218(1)	5 679(4)	1 580(3)
O(1)	506(3)	1 340(11)	1 592(7)
O(2)	1 628(3)	3 889(12)	3 081(6)
O(3)	1 133(3)	2 706(10)	1 614(6)
C(1)	155(4)	2 488(16)	−659(10)
C(2)	−134(4)	2 930(16)	−1 423(9)
C(3)	−194(4)	4 157(19)	−1 656(10)
C(4)	−468(5)	4 543(19)	−2 393(12)
C(5)	−698(5)	3 646(23)	−2 952(10)
C(6)	−639(5)	2 420(23)	−2 727(12)
C(7)	−368(5)	2 053(17)	−1 995(10)
C(8)	1 269(4)	89(15)	484(10)
C(9)	1 549(4)	−726(15)	356(11)
C(10)	1 702(5)	−1 687(16)	901(13)
C(11)	1 970(6)	−2 469(21)	769(16)
C(12)	2 058(5)	−2 333(20)	74(16)
C(13)	1 898(6)	−1 328(23)	−490(16)
C(14)	1 634(5)	−602(20)	−382(14)
C(15)	2 264(4)	3 055(17)	1 847(10)
C(16)	2 572(4)	2 709(16)	1 599(10)
C(17)	2 884(4)	3 455(18)	1 879(10)
C(18)	3 191(5)	3 169(21)	1 660(11)
C(19)	3 185(5)	2 071(22)	1 228(12)
C(20)	2 884(5)	1 396(19)	941(12)
C(21)	2 576(5)	1 655(17)	1 138(10)
C(22)	1 197(4)	5 484(14)	566(9)
C(23)	983(4)	6 361(14)	−111(9)
C(24)	1 070(4)	6 588(17)	−822(10)
C(25)	873(5)	7 395(17)	−1 461(10)
C(26)	567(5)	7 939(16)	−1 408(11)
C(27)	455(5)	7 691(16)	−742(11)
C(28)	672(4)	6 921(18)	−88(10)

TABLE 2

Atomic co-ordinates (× 10^4; H, × 10^3) for $[\mathrm{Mo^{IV}O(S_2CPh)(S_3CPh)}]$ (2), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mo	1 401.2(2)	2 591.2(3)	2 013.1(2)
S(1)	2 532.0(6)	4 037(1)	3 181.5(7)
S(2)	1 894.2(6)	4 295(1)	850.7(7)
S(3)	−36.2(5)	2 948(1)	815.7(6)
S(4)	671.8(6)	2 781(1)	3 395.2(6)
S(5)	−648.4(6)	2 378(1)	2 768.5(6)
O	1 652(2)	688(3)	1 881(2)
C(6)	−832(2)	2 605(3)	1 468(2)
C(7)	−1 753(2)	2 492(3)	854(2)
C(8)	−2 434(2)	3 184(4)	1 213(3)
C(9)	−3 295(2)	3 093(5)	618(3)
C(10)	−3 496(2)	2 281(5)	−327(3)
C(11)	−2 828(2)	1 560(5)	−680(3)
C(12)	−1 959(2)	1 670(4)	−96(2)
C(13)	2 685(2)	3 634(4)	1 936(3)
C(14)	3 459(2)	2 675(4)	1 814(3)
C(15)	3 700(2)	2 687(5)	873(3)
C(16)	4 436(3)	1 830(6)	766(3)
C(17)	4 930(2)	984(5)	1 588(4)
C(18)	4 689(2)	922(5)	2 523(3)
C(19)	3 961(2)	1 777(5)	2 646(3)
HC(8)	−231(2)	383(4)	183(2)
HC(9)	−372(3)	364(5)	84(3)
HC(10)	−410(3)	218(5)	−73(3)
HC(11)	−298(2)	106(5)	−134(3)
HC(12)	−150(2)	117(5)	−28(3)
HC(15)	336(2)	320(4)	25(3)
HC(16)	461(3)	193(6)	11(4)
HC(17)	542(3)	35(6)	154(3)
HC(18)	500(2)	27(5)	310(3)
HC(19)	376(2)	173(4)	329(2)

give the final atomic co-ordinates with standard deviations for (1) and (2) respectively. Observed and calculated structure factors and atomic thermal parameters are listed in Supplementary Publication No. SUP 23178 (12 pp.).*

Crystallographic calculations were performed on FACOM 270/20 and 230/38 computers at the Information Processing Research Centre, Kwansei Gakuin University and on an ACOS 700S computer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University. Figures 1—4 were drawn on a NUMERICON 7000 system at the Crystallographic Research Centre with a local version of ORTEP-II.†

RESULTS AND DISCUSSION

Molecular Structure of (1).—Figure 1 illustrates the molecular geometry of (1) together with the atom-labelling scheme. A stereoview of the packing of the molecules in the unit cell is given in Figure 2. The relevant bond distances and angles are listed in Table 3.

There are no unduly short intermolecular contacts in the unit cell. Two molybdenum atoms are bonded through the bridging oxygen atom. Each molybdenum atom is bound to four sulphur and two oxygen atoms to form a distorted octahedron. The Mo(1)–S(4) and Mo(2)–S(7) distances are significantly longer than the other Mo–S distances, indicating a remarkable *trans* influence of the terminal oxo-group, which has been observed in three complexes of the $[\mathrm{Mo^V{}_2O_3L_4}]$ type (L = $\mathrm{S_2COEt}$,[12] $\mathrm{S_2CNPr^n{}_2}$,[13] and $\mathrm{S_2CSPr^i}$ [14]). A terminal oxo-group is located in a *cis* position to another oxo-group with respect to the Mo–O–Mo linkage. This geometry is quite similar to those of the three $[\mathrm{Mo^V{}_2O_3L_4}]$ complexes. It is, however, noted that the Mo–O–Mo angle in the present complex [166.9(7)°] is less than those in the other $[\mathrm{Mo_2O_3L_4}]$ complexes (170—178°) reported so far.[12-14]

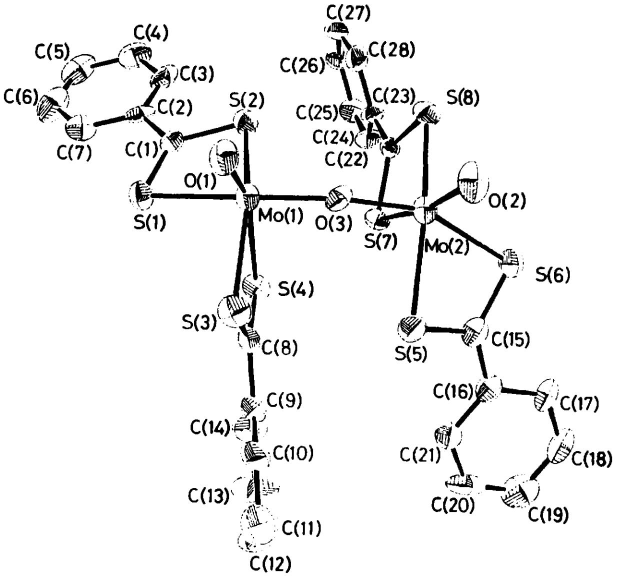

FIGURE 1 Perspective view of the molecular structure of $[\mathrm{Mo^V{}_2O_3(S_2CPh)_4}]$ (1), together with the atom-labelling scheme. Hydrogen atoms are not illustrated. Thermal ellipsoids are drawn at the 30% probability level

The bond distances between the bridging oxygen and molybdenum atoms [1.872(9), 1.869(10) Å] are somewhat larger than either of those of $[\mathrm{Mo^V{}_2O_3(S_2COEt)_4}]$ [1.851(34), 1.872(34) Å], $[\mathrm{Mo^V{}_2O_3(S_2CNPr^n{}_2)_4}]$ [1.856(13), 1.870(13) Å], and $[\mathrm{Mo^V{}_2O_3(S_2CSPr^i)_4}]$ [1.844(14) Å].

TABLE 3

Intramolecular bond distances and angles for $[\mathrm{Mo^V{}_2O_3(S_2CPh)_4}]$ (1), with estimated standard deviations in parentheses

(*a*) Distances (Å)

Mo(1)–O(1)	1.67(1)	S(5)–C(15)	1.72(2)
Mo(2)–O(2)	1.68(1)	S(6)–C(15)	1.68(2)
Mo(1)–O(3)	1.872(9)	S(7)–C(22)	1.66(2)
Mo(2)–O(3)	1.869(10)	S(8)–C(22)	1.69(2)
Mo(1)–S(1)	2.515(4)	C(1)–C(2)	1.44(2)
Mo(1)–S(2)	2.462(5)	C(8)–C(9)	1.47(2)
Mo(1)–S(3)	2.479(5)	C(15)–C(16)	1.45(2)
Mo(1)–S(4)	2.698(6)	C(22)–C(23)	1.48(2)
Mo(2)–S(5)	2.463(5)	C–C [C(2)—C(7) phenyl ring]	
Mo(2)–S(6)	2.528(5)	mean *	1.38(1)
Mo(2)–S(7)	2.722(5)	C–C [C(9)—C(14) phenyl ring]	
Mo(2)–S(8)	2.464(5)	mean *	1.38(1)
S(1)–C(1)	1.69(2)	C–C [C(16)—C(21) phenyl ring]	
S(2)–C(1)	1.70(2)	mean *	1.37(1)
S(3)–C(8)	1.69(2)	C–C [C(23)—C(28) phenyl ring]	
S(4)–C(8)	1.67(2)	mean *	1.371(5)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

† C. K. Johnson, ORTEP-II, Report ORNL5138, Oak Ridge National Laboratory, Tennessee, 1976.

TABLE 3 (*continued*)

(*b*) Selected bond angles (°)

Mo(1)–O(3)–Mo(2)	166.9(7)	O(2)–Mo(2)–O(3)	105.0(6)
O(1)–Mo(1)–O(3)	106.4(5)	O(2)–Mo(2)–S(5)	111.1(5)
O(1)–Mo(1)–S(1)	95.8(4)	O(2)–Mo(2)–S(6)	96.5(5)
O(1)–Mo(1)–S(2)	107.9(4)	O(2)–Mo(2)–S(7)	159.7(5)
O(1)–Mo(1)–S(3)	93.9(4)	O(2)–Mo(2)–S(8)	95.2(5)
O(1)–Mo(1)–S(4)	159.0(4)	O(3)–Mo(2)–S(5)	90.6(4)
O(3)–Mo(1)–S(1)	154.9(4)	O(3)–Mo(2)–S(6)	155.1(4)
O(3)–Mo(1)–S(2)	91.6(3)	O(3)–Mo(2)–S(7)	85.8(3)
O(3)–Mo(1)–S(3)	95.4(3)	O(3)–Mo(2)–S(8)	94.0(3)
O(3)–Mo(1)–S(4)	85.4(4)	S(5)–Mo(2)–S(6)	69.7(2)
S(1)–Mo(1)–S(2)	70.0(2)	S(5)–Mo(2)–S(7)	85.6(2)
S(1)–Mo(1)–S(3)	94.7(2)	S(5)–Mo(2)–S(8)	151.2(2)
S(1)–Mo(1)–S(4)	77.5(2)	S(6)–Mo(2)–S(7)	77.8(2)
S(2)–Mo(1)–S(3)	154.1(2)	S(6)–Mo(2)–S(8)	96.5(2)
S(2)–Mo(1)–S(4)	88.7(2)	S(7)–Mo(2)–S(8)	66.6(2)
S(3)–Mo(1)–S(4)	67.2(2)	Mo(2)–S(5)–C(15)	88.6(6)
Mo(1)–S(1)–C(1)	87.0(5)	Mo(2)–S(6)–C(15)	87.2(6)
Mo(1)–S(2)–C(1)	88.3(6)	Mo(2)–S(7)–C(22)	83.9(5)
Mo(1)–S(3)–C(8)	90.9(6)	Mo(2)–S(8)–C(22)	92.1(5)
Mo(1)–S(4)–C(8)	84.2(7)	S(5)–C(15)–S(6)	113.8(11)
S(1)–C(1)–S(2)	114.7(8)	S(7)–C(22)–S(8)	117.1(8)
S(3)–C(8)–S(4)	117.4(10)		

* Defined as $\Sigma w_i y_i / \Sigma w_i$, where y_i is an individual C–C distance and w_i is the squared reciprocal of its standard deviation. The standard deviation of the mean is defined as $\{\Sigma w_i (y_i - \bar{y})^2 / [(n - 1)\Sigma w_i]\}^{\frac{1}{2}}$.

Furthermore, O(1) and O(2) deviate by 0.04 and 0.19 Å respectively from the Mo(1)–O(3)–Mo(2) plane. These findings predict a rather unstable Mo–O–Mo linkage of the present complex. This is consistent with the fact that the present complex readily disproportionates to oxomolybdenum(IV) and dioxomolybdenum(VI) complexes in solution, as will be mentioned later.

Molecular Structure of (2).—Figure 3 shows the molecular structure of (2) together with the atom-labelling scheme. A stereoview of the packing of the molecules in the unit cell is given in Figure 4. The relevant bond distances and angles are listed in Table 4.

TABLE 4

Intramolecular bond distances and angles for [$Mo^{IV}O(S_2CPh)(S_3CPh)$] (2), with estimated standard deviations in parentheses

(*a*) Distances (Å)

Mo–S(1)	2.368(1)	S(4)–S(5)	2.048(1)
Mo–S(2)	2.361(1)	S(5)–C(6)	1.670(3)
Mo–S(3)	2.416(1)	C(6)–C(7)	1.466(4)
Mo–S(4)	2.376(1)	C(13)–C(14)	1.496(5)
Mo–O	1.673(2)	C–C [C(7)—C(12) phenyl ring] mean *	1.386(3)
Mo–C(13)	2.215(3)	C–C [C(14)—C(19) phenyl ring] mean *	1.385(6)
S(1)–C(13)	1.744(4)		
S(2)–C(13)	1.728(3)		
S(3)–C(6)	1.700(3)		

(*b*) Selected bond angles (°)

O–Mo–S(1)	114.0(1)	S(4)–Mo–C(13)	128.3(1)
O–Mo–S(2)	113.3(1)	Mo–S(1)–C(13)	63.1(1)
O–Mo–S(3)	104.8(1)	Mo–S(2)–C(13)	63.4(1)
O–Mo–S(4)	108.3(1)	Mo–S(3)–C(6)	109.1(1)
O–Mo–C(13)	98.0(1)	Mo–S(4)–S(5)	107.96(4)
S(1)–Mo–S(2)	78.10(3)	Mo–C(13)–S(1)	72.4(1)
S(1)–Mo–S(3)	141.12(4)	Mo–C(13)–S(2)	72.4(1)
S(1)–Mo–S(4)	83.85(3)	Mo–C(13)–C(14)	123.7(2)
S(1)–Mo–C(13)	44.6(1)	S(1)–C(13)–C(14)	120.6(2)
S(2)–Mo–S(3)	84.47(3)	S(2)–C(13)–C(14)	121.2(2)
S(2)–Mo–S(4)	138.43(4)	S(3)–C(6)–S(5)	125.0(2)
S(2)–Mo–C(13)	44.2(1)	S(3)–C(6)–C(7)	118.3(2)
S(3)–Mo–S(4)	86.77(3)	S(5)–C(6)–C(7)	116.7(2)
S(3)–Mo–C(13)	128.7(1)	S(4)–S(5)–C(6)	106.8(1)

* Defined as $\Sigma w_i y_i / \Sigma w_i$, where y_i is an individual C–C distance and w_i is the squared reciprocal of its standard deviation. The standard deviation of the mean is defined as $\{\Sigma w_i (y_i - \bar{y})^2 / [(n - 1)\Sigma w_i]\}^{\frac{1}{2}}$.

The crystal structure consists of four discrete monomers in the unit cell. The oxomolybdenum group is co-

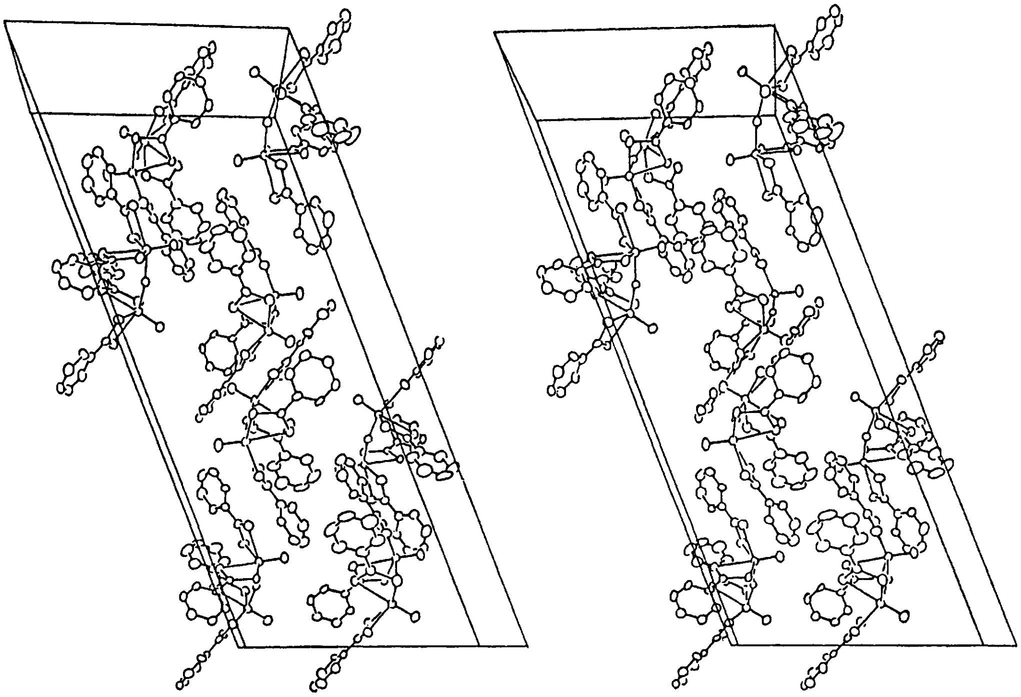


FIGURE 2 Stereoview of a unit cell of [$Mo^{V}{}_2O_3(S_2CPh)_4$]. The origin of the cell is at the bottom left corner. The z axis is horizontal, the x axis vertical, and the y axis points out from the origin

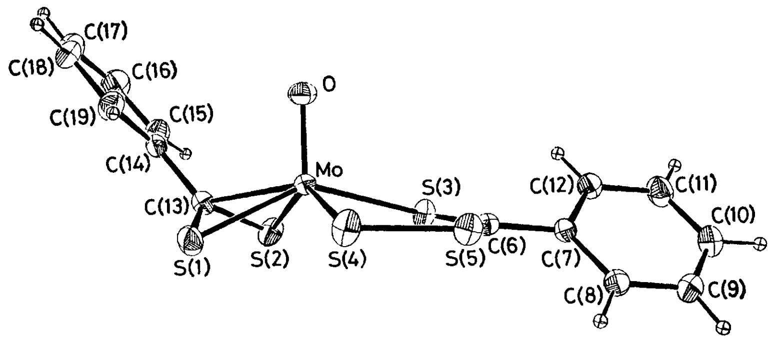


FIGURE 3 Perspective view of the molecular structure of $[\mathrm{Mo^{IV}O(S_2CPh)(S_3CPh)}]$ (2), giving the atom-labelling scheme. Thermal ellipsoids are drawn at the 30% probability level except those for hydrogen atoms, which are illustrated by spheres with an arbitrary radius

ordinated to both dithiobenzoato- and trithioperoxybenzoato-ligands. This is the first molybdenum complex of trithioperoxybenzoate, although zinc(II), nickel(II), palladium(II), and platinum(II) complexes containing trithioperoxyarylato-ligands have been reported.[15,16] The geometry around molybdenum is a distorted square pyramid; the S(1), S(2), S(3), and S(4) atoms form an approximate square basal plane and the molybdenum is located 0.81 Å above the plane. The C(13) atom 0.69 Å above this plane approaches very close to molybdenum [Mo–C(13) 2.215(3) Å], indicating η^3 co-ordination of the S_2CPh ligand to molybdenum through C(13) as well as S(1) and S(2). A similar mode of co-ordination of the CS_2 moiety to molybdenum has recently been reported for bis(*S*-isopropyl trithiocarbonato)oxomolybdenum(IV) [Mo–C 2.25(1) Å].[4] The sterically strained η^3 co-ordination may be the origin of the significantly reduced S(1)–Mo–S(2) angle [78.10(3)°] compared with the usual angle of 90°, while the S(3)–Mo–S(4) angle [86.77(3)°] is close to the usual value.

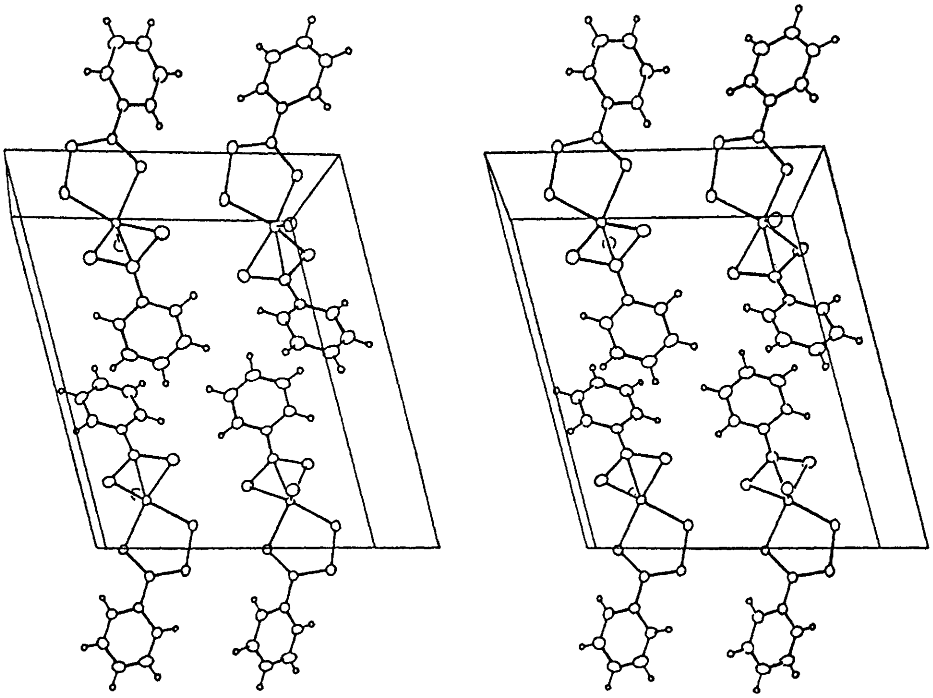
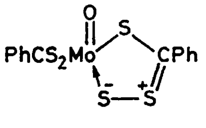


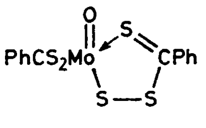
FIGURE 4 Stereoview of a unit cell of $[\mathrm{Mo^{IV}O(S_2CPh)(S_3CPh)}]$. The origin of the cell is at the bottom left corner. The y axis is horizontal, the z axis vertical, and the x axis points out from the origin

The S(3), S(4), S(5), and C(6) atoms are approximately coplanar, molybdenum being located 0.56 Å out of this plane. The five-membered chelate ring contains a normal[17] S–S single bond [S(4)–S(5) 2.048(1) Å], although this is somewhat longer than those of bis(trithioperoxybenzoato)nickel(II) [2.022(3) Å], bis(trithioperoxybenzoato)zinc(II) [2.007(3) Å],[15] bis(trithioperoxycumato)zinc(II) [2.008(14) Å], and dithiocumato(trithioperoxycumato)nickel(II) [2.016(4) Å] (cumate = *p*-isopropylbenzoate).[16] It should be noted that the S(3)–C(6) distance [1.700(3) Å] of the present complex is significantly longer than the S(5)–C(6) distance [1.670(3) Å].

This is in contrast with the nickel(II) and zinc(II) complexes, in which the S–C bond of the trithioperoxy-ligand corresponding to the S(3)–C(6) bond is shorter than that to the S(5)–C(6) bond. Thus, the canonical structure (I) in the resonance hybrids may be preferable to (II) in the present complex.



(I)



(II)

Although the phenyl ring bound to C(13) is approximately on the C(13)–S(1)–S(2) plane, the phenyl ring attached to C(6) is twisted by 41.8° from the S(4)–S(5)–C(6)–S(3) plane. The S(3)–C(6)–S(5) angle [125.0(2)°] is large in comparison with the S(1)–C(13)–S(2) angle [118.2(2)°], which can cause repulsions between S(3) and H(12) and between S(5) and H(8) atoms, resulting in the twisted structure.

Recently, an EXAFS study on xanthine oxidase has shown that there exists a rather long Mo–S bond (2.84 Å) in addition to the short ones (2.16, 2.52, and 2.54 Å), suggesting that the distant sulphur may be considered as the second sulphur of a persulphide ligand.[2] In the present complex, however, no significant interaction between Mo and S(5) (3.58 Å) is observed.

Properties of (1) *in Solution*.—The i.r. spectrum of (1) in a Nujol mull shows three sharp bands in the 930—950 cm^{-1} region [Figure 5(*a*)], of which the lowest-frequency band (933 cm^{-1}) may be due to ν(C–S), since the wavenumber is coincident with that of a strong absorption observed for [Mo^{IV}O(S$_2$CPh)$_2$]. Either or both of the remaining bands, at 940 and 947 cm^{-1}, may be assigned to ν(Mo=O) of (1) by reference to the i.r. spectra of several [Mo$^{V}_2$O$_3$L$_4$] complexes which show an intense ν(Mo=O) band in the 920—980 cm^{-1} region.[1] These two bands, however, disappeared in the solution spectrum of (1) in dibromomethane, while that at 933 cm^{-1} remained. Instead, immediately after dissolution, the spectrum displayed three new intense absorptions at 970, 922, and 893 cm^{-1} [Figure 5(*b*)]. That at 970 cm^{-1} is reasonably assigned to ν(Mo=O) of [Mo^{IV}O(S$_2$CPh)$_2$] which is formed by disproportionation of (1) in solution. This assignment suggests the concomitant formation of [Mo^{VI}O$_2$(S$_2$CPh)$_2$] in dibromomethane according to equation (i).

$$[\mathrm{Mo^{V}_2O_3(S_2CPh)_4}]\ (1) \rightleftharpoons [\mathrm{Mo^{IV}O(S_2CPh)_2}] + [\mathrm{Mo^{VI}O_2(S_2CPh)_2}] \quad \text{(i)}$$

Thus, the bands at 922 and 893 cm^{-1} may be assigned to ν(Mo=O) of [Mo^{VI}O$_2$(S$_2$CPh)$_2$]. Similar disproportionation equilibria were reported for [Mo$^{V}_2$O$_3$L$_4$], where L = S$_2$CNEt$_2$,[18,19] S$_2$PPh$_2$,[20] and S$_2$CSPr^i.[4,21] In the present molybdenum(V) complex, however, the equilibrium seems to lie so far to the right in dibromomethane at ambient temperature, since the ν(Mo=O) bands at 940 and/or 947 cm^{-1} almost disappear.

It should be noted that the solution spectrum of (1) is time-dependent as depicted in Figure 5(*b*); the two lower-frequency ν(Mo=O) bands weaken with time, whilst the highest-frequency band becomes stronger. Eventually, the first two bands completely disappear. This indicates that [Mo^{VI}O$_2$(S$_2$CPh)$_2$] is unstable to decomposition in dibromomethane, giving more [Mo^{IV}O(S$_2$CPh)$_2$]. A similar degradation in solution was reported for [Mo^{VI}O$_2$(S$_2$CSPr^i)$_2$].[21]

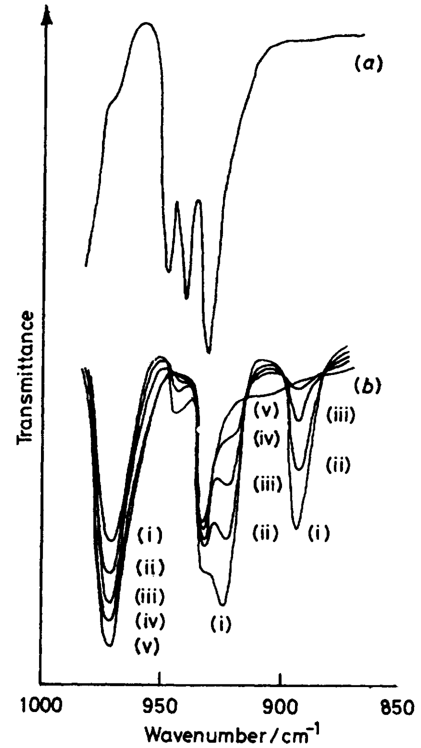


FIGURE 5 Infrared spectra of [Mo$^{V}_2$O$_3$(S$_2$CPh)$_4$], (1), in Nujol mulls (*a*) and the change with time after dissolving in dibromomethane at room temperature (*b*): (i) 3, (ii) 12, (iii) 21, (iv) 30 min, and (v) infinity

Figure 6 illustrates the electronic spectra of (1) in the solid state and in solution. The solid-state spectrum

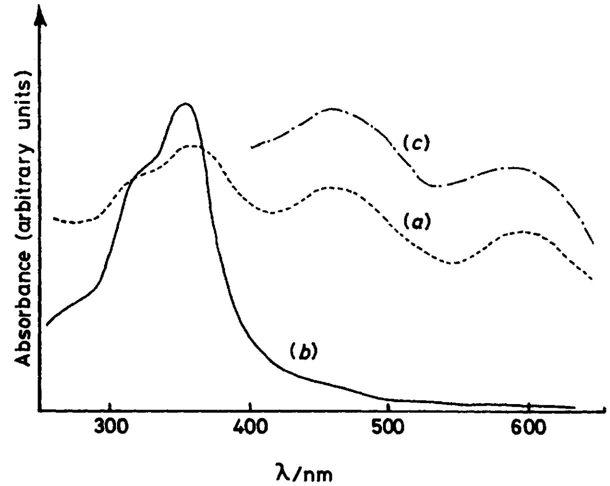


FIGURE 6 Electronic spectra of [Mo$^{V}_2$O$_3$(S$_2$CPh)$_4$] (1), in Nujol mulls (*a*), in 1,2-dichloroethane at 25 °C (*b*), and in carbon disulphide at −60 °C (*c*)

in the visible region shows two absorption maxima at 460 and 608 nm. These bands almost disappear in 1,2-dichloroethane solution at room temperature. This is consistent with the disproportionation of (1) into $[Mo^{IV}O(S_2CPh)_2]$ and $[Mo^{VI}O_2(S_2CPh)_2]$ in solution, as described above for the i.r. spectra. On the other hand, the solution spectrum in carbon disulphide at −60 °C shows two absorption maxima with the same wavenumbers as those observed in the solid-state spectrum, indicating that the above mentioned equilibrium lies over to the left in this solvent at low temperatures.

Isolation and Properties of (2).—Compound (2) was isolated not only by chromatography, but also from recrystallization of a green precipitate obtained by the reaction of $Na_2[MoO_4]$ with $[NEt_2H_2][S_2CPh]$ in an acidic aqueous medium. The i.r. spectrum of the precipitate in a Nujol mull showed the presence of (1) as the main component and $[Mo^{IV}(S_2CPh)_4]$, $[Mo^{VI}O_2(S_2CPh)_2]$, and $(PhCS_2)_2$ as minor ones. Shortly (3 min) after the precipitate was dissolved in dibromomethane, however, the solution displayed an i.r. band at 958 cm^{-1} due to the ν(Mo=O) vibration of (2). It is well known that organic disulphides react with electro- or nucleophiles and undergo S–S bond cleavage.[22] Thus, $(PhCS_2)_2$ presumably acts as a sulphur source, producing the S_3CPh ligand in the reaction with the S_2CPh ligand. We have confirmed that $(PhCS_2)_2$ reacts with $[Mo^{IV}O(S_2CPh)_2]$ in dichloromethane to give (2), although the rate of reaction is very slow. Another possible route to (2) may be the decomposition of unstable $[Mo^{VI}O_2(S_2CPh)_2]$ formed by disproportionation of (1) in solution, followed by the formation of any species acting as a sulphur source. In fact, 2 d after (1) was dissolved in dibromomethane, the i.r. bands due to (2) were detectable.

The ^{13}C n.m.r. spectrum of (2) in $[^2H_1]$chloroform exhibited a signal at δ 233.9 p.p.m. and nine signals in the region δ 126—143 p.p.m. The signal at extremely low field can be reasonably assigned to the CS_3 carbon nucleus, since the CS_2 signal of $PhCS_2Et$ was observed at δ 228.6 p.p.m. in $[^2H_1]$chloroform.[23] Of the signals observed in the region δ 126—143 p.p.m., eight can be assigned to carbons of the two non-equivalent phenyl rings and the remaining one to the CS_2 carbon nucleus. The occurrence of the CS_2 signal at such high field appears to be due to the shielding effect of the molybdenum atom, assuming the existence of the η^3-co-ordinating CS_2 moiety even in solution.

The electronic spectra of (2) in $CHCl_3$ showed two intense maxima at 330 (ε = 25 000) and 406 nm (9 800 dm^3 mol^{-1} cm^{-1}). These bands are tentatively assigned to internal-ligand transitions, since $[Mo^{IV}O(S_2CPh)_2]$ exhibits maxima at 320 (sh), 353 (33 000), and 465 (sh) nm and $[Ni^{II}(S_2CPh)(S_3CPh)]$ displayed intense bands at 337 (54 000) and 439 nm (3 700) in chloroform.[24] No *d–d* band, however, was detected for (2), although $[Mo^{IV}O(S_2CPh)_2]$ exhibits a weak *d–d* band at 530 nm (680).

The equimolar reaction of (2) with PPh_3 in dichloromethane at room temperature gave $[Mo^{IV}O(S_2CPh)_2]$ and PPh_3S. A sulphur-abstraction reaction of this type was also reported for $[M^{II}(S_2CC_6H_4Pr^i\text{-}p)(S_3CC_6H_4Pr^i\text{-}p)]$ (M = Zn or Ni).[16] Moreover, (2) reacted with a large excess of PR_3 (R = Ph or Bu^n) to afford $[Mo^{IV}O(S_2CPh)_2(PR_3)]$, which can also be obtained from an equimolar reaction of $[Mo^{IV}O(S_2CPh)_2]$ and PR_3 in dichloromethane.

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